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CITATION:

Miyake, Masao ...[et al]. Electrodeposition of purified aluminum coatings from dimethylsulfone-AlCl electrolytes with trimethylamine hydrochloride. Surface and Coatings Technology 2012, 206(19-20): 4225-4229

ISSUE DATE:

2012-05-25

URL:

http://hdl.handle.net/2433/237630

Electrodeposition of purified aluminum coatings from dimethylsulfone-$AlCl_3$ electrolytes with trimethylamine hydrochloride

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Abstract

Aluminum (Al) coatings have been electrodeposited from dimethylsulfone ($DMSO_2$)-$AlCl_3$ electrolytes, but the coatings usually contained trace amounts of chlorine (Cl) and sulfur (S) as impurities. Since these impurities make the coatings hard and brittle, and moreover may adversely affect the corrosion- and oxidation-resistances of the Al coatings, it would be desirable to decrease their contents in the Al coatings. Examination of the Al coatings electrodeposited from the electrolytes with the addition of various amounts of trimethylamine hydrochloride (TMA) revealed that the Cl and S contents of the Al coatings decreased with increasing concentration of TMA in the electrolyte. The addition of TMA also brought about changes in the surface morphology and crystal orientation of the Al coatings. Preferential adsorption of TMA on the surface of the Al deposit was inferred to be a cause of the exclusion of Cl and S from the Al coating. As a result of the decrease in Cl and S contents, the Al coatings were softened.

Keywords

Electroplating, Organic solvent, Impurity control

1. Introduction

Aluminum (Al) offers good corrosion-resistance owing to its protective oxide layer, and therefore can be used as a corrosion-resistant coating for metallic materials. Several methods are available to form Al coatings, including hot dipping [1], thermal spraying [2], vapor phase deposition [3] and electrodeposition. Among them, electrodeposition offers many advantages, such as low cost, simple operation, and easy control of the coating thickness. The electrodeposition of Al, however, cannot occur in aqueous solutions, and thus requires non-aqueous solvents [4-7]. One of the electrolytes available for Al electrodeposition is dimethylsulfone ($DMSO_2$)-$AlCl_3$. Compared with other media such as inorganic molten salts [5] and ionic liquids [6-8], the $DMSO_2$-$AlCl_3$ electrolyte has merits that the chemicals are cheap and easy in handling. We have succeeded in obtaining uniform, smooth Al coatings by electrodeposition from $DMSO_2$-$AlCl_3$ electrolytes [9-11]. Furthermore, fabrication of aluminide layers which exhibit high oxidation-resistance at high temperatures was demonstrated by electrodeposition and subsequent annealing [10-12].

In the $DMSO_2$-$AlCl_3$ electrolytes, $AlCl_3$ reacts with $DMSO_2$ according to:

$$4AlCl_3 + 3DMSO_2 \rightarrow Al(DMSO_2)_3^{3+} + 3AlCl_4^-,$$

and the electrodeposition of Al can occur from $Al(DMSO_2)_3^{3+}$ [13]. The Al coatings electrodeposited from the $DMSO_2$-$AlCl_3$ electrolytes, however, contain chlorine (Cl) and sulfur (S) as impurities, because the electrolytes include Cl as $AlCl_4^-$ and S as $DMSO_2$. These

impurities make the Al coatings hard and brittle. Moreover, they may have an adverse effect on the corrosion- and oxidation-resistances. Hence, it would be desirable to decrease the contents of these impurities. It has been reported that the incorporation of the impurities could be suppressed by adding di- or trimethylamine hydrochloride ($(CH_3)_nNH_{(3-n)}$•HCl, n = 2 or 3) to the electrolyte [14, 15]. However, the optimum amount of the additives and the mechanisms of the impurity exclusion have not previously been elucidated. In this study, the Al coatings electrodeposited from $DMSO_2$-$AlCl_3$ electrolytes containing various amounts of trimethylamine hydrochloride (TMA) were examined for impurity contents and morphology to obtain a better insight into the mechanism of the electrodeposition of purified Al coatings. The effect of TMA on the hardness of the resulting coatings was also examined.

2. Experimental

2.1 Electrodeposition

Preparation of the electrolytic bath and electrodeposition of Al were carried out in an Ar-filled glove box equipped with a circulation system. $DMSO_2$ (Tokyo Chemical Industry, 99%) and anhydrous $AlCl_3$ grains (Fluka, crystallized, 99%) were used as the solvent and Al source, respectively. Trimethylamine hydrochloride (TMA, Sigma-Aldrich, 99%) was added to the electrolyte as an additive. The $DMSO_2$ and the TMA were used after drying for 24 h at 60 °C, respectively. $AlCl_3$ had been stored in the glove box and was used as received. The mol

ratio of $DMSO_2$ to $AlCl_3$ in the electrolyte was 10 : 2 or 10 : 3. The content of TMA in the electrolyte was 0-0.4 mol with respect to 10 mol of $DMSO_2$. The water content of the $DMSO_2$-$AlCl_3$ electrolyte was determined to be 0.04-0.06% by a coulometric Karl-Fischer method (MKC-510 N; Kyoto Electronics Manufacturing Co., Ltd). A glass vessel with a volume of 150 mL was used as an electrochemical cell. A copper plate (Nilaco, 99%) and an Al plate (Nilaco, 99%) were used as the substrate and counter electrode, respectively. A part of the copper plate was covered with PTFE tape so that only a certain area (10 x 10 mm^2) would be exposed. Galvanostatic electrodeposition was performed with an electrochemical analyzer (ALS, model 660 C) at a current density of 20-80 mA cm^{-2}. The temperature of the electrolyte was maintained at 110 °C by a thermostat. The electrolyte was stirred by a magnetic stirrer at 80 rpm during the electrochemical reactions. The thickness of the resulting Al coatings was in the range from 30 to 50 μm. After the electrodeposition, the Al coating was washed with copious distilled water.

2.2 Characterization

The contents of Cl and S in electrodeposited Al coatings were determined by X-ray fluorescence spectrometry (XRF; Shimadzu, XRF-1500). X-ray photoelectron spectroscopy (XPS; Kratos Analytical, ESCA-3400 system) was carried out to examine the contents and chemical states of Cl and S. The XPS was performed using a Mg-Kα X-ray source with Ar+

ion etching at a rate of approximately 0.5 nm/min, which was determined from a SiO_2 standard film. The XPS spectra obtained were calibrated so that C 1s peak position from hydrocarbons would be 285.0 eV. The surface morphology and crystal orientation of the Al coatings were examined by scanning electron microscope (SEM; Hitachi S-3500) and X-ray diffraction (XRD; PANalytical, X'Pert PRO-MPD), respectively. The Vickers hardness of the Al coatings was determined with a micro hardness tester (Shimadzu, HMV-1) by setting the required load at 98.07 mN. Before the XRF and Vickers hardness test, the surface of each Al coating was polished with SiC paper to eliminate the influence of any electrolyte residues. The XPS, XRD and SEM observations were carried out for the coatings just after washing with distilled water.

3. Results

3.1. Impurity incorporation from the electrolyte without TMA

Before investigating the effects of TMA, the impurity contents of Al coatings electrodeposited from the $DMSO_2$-$AlCl_3$ electrolytes without any additives were determined by XRF. The main impurities of the coatings were O, C, Cl and S. We focused only on Cl and S in this study, since the inclusion of Cl and S is characteristic of coatings electrodeposited from the $DMSO_2$-$AlCl_3$ electrolytes. Figure 1 shows the Cl and S contents of the Al coatings electrodeposited at various current densities from the electrolytes with two different

compositions ($DMSO_2$: $AlCl_3$ = 10 : 3 and 10 : 2) without additives. Electrodeposition at higher current densities produced Al coatings with lower contents of Cl and S. However, electrodeposition at a higher current density than 100 mA cm^{-2} resulted in a rough, black deposit. The Cl and S contents also slightly depended on the composition of the electrolyte; they were lower in the coatings from the electrolyte of $DMSO_2$: $AlCl_3$ = 10 : 2. As shown in the inset of Fig. 1, the mol ratios of Cl to S in the Al coatings varied depending on the current density, implying that the impurity incorporation was not caused only by a random inclusion of the electrolyte into the Al deposit.

XPS analysis with Ar^+ ion etching was performed for the Al coatings to examine the chemical state and distribution of the impurities in the coatings. A representative set of XPS spectra of Cl 2p, S 2p and S 2s regions is shown in Fig. 2. A signal was detected at ~199 eV, which agrees with the Cl $2p_{3/2}$ binding energies for many chlorides. This signal declined with increasing Ar etching time, but did not disappear, confirming that the Cl was not just a surface contaminant, but rather was incorporated into the Al coating during the electrodeposition. As for S, an S 2p signal was detected at ~169.3 eV from the surface of the Al coating before the Ar etching. The peak position is almost in agreement with the reported value for $DMSO_2$ (169.2 eV) [16], showing the presence of $DMSO_2$ on the surface of the Al coating. This signal, however, diminished with increasing etching time and disappeared after etching for 102 ks, indicating that the $DMSO_2$ was present only as a surface residue. The broad peak over the

range of 160-170 eV is a plasmon-loss satellite of the Al 2s peak [17], which emerged only after the surface oxide layer of the Al coating was removed by the Ar etching. If S is present as sulfides or elemental S, their signals should appear in the range of 160-165 eV [18], but they are obscured by the Al satellite peak. Hence, the S 2s region needs to be analyzed to clarify whether S is present in other forms than $DMSO_2$. In the S 2s region, a signal was observed at 233.2 eV from the surface of the Al coating. According to the above speciation using the S 2p signal, this signal should be due to residual $DMSO_2$, and therefore should disappear after the etching. The disappearance, however, could not be observed clearly, because Ar $2p_{3/2}$ satellites derived by Mg-K$\alpha_{3,4}$ radiation arose at ~233 eV and overlaid the signal of $DMSO_2$ after the Ar etching started. Another signal was found at a lower binding energy (226 eV) after the Ar etching. This signal is ascribed to a sulfide in the coating, since many sulfides are reported to give a signal at around 226 eV [19, 20]. The signal at 226 eV remained even after etching for 102 ks, showing that S was incorporated in the Al coating during electrodeposition as a sulfide.

3.2. Effect of TMA on impurity contents and morphology

Electrodeposition of Al was carried out in electrolytes of $DMSO_2$: $AlCl_3$ = 10 : 3 containing 0-0.4 mol TMA at a constant current density of 60 mA cm^{-2} to clarify the effect of TMA on impurity incorporation. Figure 3 plots the Cl and S contents of the Al coatings

determined by XRF against the TMA content in the electrolyte. While the Al coatings from the electrolyte without TMA contained ~0.4 at.% Cl and S, both the contents decreased with increasing content of TMA in the electrolyte. The decrease leveled off when the amount of TMA was 0.2 mol, at which point the Cl and S contents were below 0.1 at%.

The XPS spectra for the Al coatings electrodeposited in the presence of TMA (Fig. 4) were qualitatively the same as those for the coating without TMA (Fig. 2), except that the signals of Cl and S disappeared after the long-time Ar etching. Although impurities derived from TMA could be included in the Al coatings, our XPS system could not provide evidence of this because of high noise levels in the signals of carbon and nitrogen.

The Cl and S contents of the coatings determined by the XPS analysis are plotted against etching time in Fig. 5, comparing the results for the coatings without and with TMA. In this graph, sums of the S contents derived from the S 2p signal at 169 eV and S 2s signal at 233 eV are shown. Before and at the beginning of the etching, higher contents of Cl and S were observed because of surface contamination by the residue of the electrolyte. Even after the contaminated surface layer was etched away, both the Cl and S contents of the Al coating without TMA stayed almost constant at ~0.2 at.%, which is in agreement with that determined by XRF (~0.4 at.%) within experimental error. In contrast, the Cl and S contents of the coating with TMA fell below the detection limit (<0.1 at.%). These profiles clearly show that Cl and S were incorporated into the Al coatings during the electrodeposition from the

electrolyte without TMA, whereas the incorporation was inhibited by the addition of TMA.

The addition of TMA also affected the surface morphology and crystal orientation of the electrodeposited Al coatings. Figure 6 presents SEM images showing the surface of the Al coatings from the electrolytes with 0-0.4 mol TMA. In the image of the Al coatings without TMA (Fig. 6a), well-faceted crystal grains of Al in the size range of 2-10 μm can be seen. According to the report by Jiang et al. [21], this faceted morphology is formed when the temperature and current density are relatively low, although nodular morphologies develop at higher temperatures and higher current densities. The addition of 0.05 mol or 0.1 mol of TMA made the grain size of Al crystals smaller; Al grains with a size of ~1□ μm appear in the SEM images (Fig 6b and 6c). The addition of a greater amount of TMA than 0.1 mol recovered the grain size of Al (Fig. 6d and 6e). However, compared with the Al grains of the coating without TMA, those with 0.2 mol and 0.4 mol TMA looks less-sharply faceted.

Figure 7 shows XRD patterns of the coatings. Each diffraction peak in Fig. 7 can be assigned to that of the Al or Cu substrate, confirming that the electrodeposited coatings are essentially composed of a single phase of metallic Al. The XRD patterns also show that the preferential crystal orientation of Al coatings varies with the content of TMA; the Al coating without TMA has no preferential orientation, while those with 0.05 and 0.1 mol TMA have a strong <111> orientation. The further addition of TMA decreases the degree of preferential orientation, and the coating from the electrolyte with 0.4 mol TMA shows an almost random

orientation again.

There is a correlation between the crystal orientation and the grain size revealed by SEM (Fig. 6); when the coatings show the <111> orientation, the Al grain size is small. However, no correlation can be found between the morphology and the contents of Cl and S in the Al coatings (Fig. 3). Hence, although the addition of TMA changes the morphology of the Al coatings, the morphological change is not the direct cause of the decrease in the impurity contents.

3.3. Hardness

Since the Cl and S contents in the Al coatings decreased by the addition of TMA, the hardness of the Al coatings was expected to decrease. Figure 8 shows the Vickers hardness of the Al coatings. The Al coatings electrodeposited in the absence of TMA had a hardness of 155 HV (= 1.52 GPa). The hardness decreased with increasing content of TMA in the electrolyte, and Al coatings with a hardness of ~60 HV were obtained when the TMA content was 0.2-0.4 mol. This tendency of decrease in the hardness corresponds to that of the Cl and S contents in the Al coatings (Fig. 3), and therefore the decrease in the impurity contents softens the coatings. Although the hardness of metallic materials generally depends on the crystal grain size, there was no correlation between the morphology and the hardness of the Al coatings in the present case; the impurities dominantly affected the hardness. The lowest

hardness number obtained in this study was a little higher than that for pure aluminum (23-30 HV) reported in the literature [22, 23].

4. Discussion

The XPS analysis suggested that S is present in the Al coatings as a state of sulfide, which is a reduced form of $DMSO_2$. Legrand et al. reported a similar sulfide formation from $DMSO_2$; they pointed out that an Al foil was corroded in a $DMSO_2$ bath in association with a reduction of $DMSO_2$ [24]. The sulfide formation from $DMSO_2$ could be a cause of the impurity incorporation into the Al coating. However, the electrochemical reduction of $DMSO_2$ does not seem to have a direct relation with the incorporation rate of S into the Al coating, because the S contents of the Al coating increased even as the cathode potential became more positive, i.e. as the current density decreased (Fig. 1).

The impurity incorporation should occur by depositing Al atoms on impurity ions or molecules adsorbed on the surface of the Al deposit. In the present case, the incorporation rate is thought to be limited by the slow adsorption of the impurity ions from the electrolyte onto the Al deposit. Since Cl is present in the electrolyte as negatively charged $AlCl_4^-$ ions, its adsorption rate onto the cathode surface must be small and further decrease as the cathode potential becomes more negative. Therefore, the hypothesis can be made that the adsorption rate of $AlCl_4^-$ onto the cathode surface limits the incorporation of Cl into the Al coating. This

hypothesis is consistent with the decrease of Cl content with increasing current density (Fig. 1). As for S, it is still not clear what specific species is the direct source of the S in the Al coating. However, since the incorporation behavior of S was similar to that of Cl (Fig. 1), the rate-limiting step of the S incorporation could also be the adsorption of S-bearing ions onto the cathode.

The variation of the crystal orientation with the concentration of TMA (Fig. 7) implies that TMA adsorbs on the surface of Al crystals during the electrodeposition. With a small amount of TMA, TMA absorbs preferentially on specific crystal planes and thereby changes the crystal growth rates in specific crystal directions, resulting in the preferentially-orientated Al crystals. On the other hand, with a large amount of TMA, TMA absorbs on all over the Al crystals, leading to an isotropic crystal growth and thus the random orientation. Endres et al., also speculated that morphological variations of the Al coatings electrodeposited from ionic liquids with different cations were caused by the adsorption of the cations on the Al deposits [8].

The decrease in the Cl and S contents by the addition of TMA can be attributed to the preferential adsorption of TMA on the surface of the Al deposit. The preferentially-adsorbed TMA restricts the $AlCl_4^-$ and S-bearing ions from being adsorbed on the cathode surface, thereby decreasing the amounts of Cl and S incorporated in the coatings. In this case, TMA could be incorporated into the Al coatings instead of Cl and S. However, even if TMA was

present in the coatings, the hardness of the Al coatings was decreased by the exclusion of Cl and S.

5. Conclusions

The Al coatings electrodeposited from the $DMSO_2$-$AlCl_3$ electrolytes without any additives contained 0.1-1 at.% of Cl and S. These impurity contents decreased with increasing deposition current density, and also depended on the $DMSO_2/AlCl_3$ ratio. XPS analysis indicated that Cl and S were incorporated in the Al coatings in the states of chloride and sulfide, respectively. The addition of TMA to the electrolyte had the effect of decreasing the incorporation of Cl and S into the Al coatings. By the addition of 0.2 mol of TMA, both the Cl and S contents decreased to below 0.1 at.%. The preferential orientation and the surface morphology of the coatings varied depending on the TMA concentration, implying that TMA was adsorbed on the surface of Al deposit during the electrodeposition. These results suggested that the incorporation rates of Cl and S were limited by the adsorption rates of $AlCl_4^-$ and S-bearing ions onto the surface of the Al deposit, and the preferential adsorption of TMA on the cathode surface prevented other ions being adsorbed, thereby decreasing the incorporation of Cl and S into the Al deposit. As a result of the decrease in the Cl and S contents, the Al coatings were softened.

Acknowledgements

The authors thank Kenji Kazumi and Teruyosi Unesaki for their assistance in SEM observation, and Yutaka Sonobayashi for the XPS measurements.

References

[1] W.-J. Cheng, C.-J. Wang, Surface & Coatings Technology 205/19 (2011) 4726.

[2] M. Campo, M. Carboneras, M.D. Lopez, B. Torres, P. Rodrigo, E. Otero, J. Rams, Surface & Coatings Technology 203/20-21 (2009) 3224.

[3] Y. Liu, L.J. Overzet, M.J. Goeckner, Thin Solid Films 510/1-2 (2006) 48.

[4] W. Simka, D. Puszczyk, G. Nawrat, Electrochimica Acta 54/23 (2009) 5307.

[5] Q.F. Li, H.A. Hjuler, R.W. Berg, N.J. Bjerrum, Journal of the Electrochemical Society 137/2 (1990) 593.

[6] J.K. Chang, S.Y. Chen, W.T. Tsai, M.J. Deng, I.W. Sun, Electrochemistry Communications 9/7 (2007) 1602.

[7] Q. Liao, W.R. Pitner, G. Stewart, C.L. Hussey, G.R. Stafford, Journal of the Electrochemical Society 144/3 (1997) 936.

[8] S.Z. El Abedin, E.M. Moustafa, R. Hempelmann, H. Natter, F. Endres, Chemphyschem 7/7 (2006) 1535.

[9] T. Hirato, J. Fransaer, J.P. Celis, Journal of the Electrochemical Society 148/4 (2001) C280.

[10] S. Shiomi, M. Miyake, T. Hirato, A. Sato, Materials Transactions 52/6 (2011) 1216.

[11] M. Miyake, S. Tajikara, T. Hirato, High Temperature Materials and Processes 30 (2011) 485.

[12] M. Miyake, S. Tajikara, T. Hirato, *Surface and Coatings Technology* 205/21-22 (2011) 5141.

[13] L. Legrand, A. Tranchant, R. Messina, F. Romain, A. Lautie, Inorganic Chemistry 35/5 (1996) 1310.

[14] H. Hoshi, A. Okamoto, S. Andoh, Hitachi Metals Technical Review 27 (2011) 20.

[15] H. Hoshi, A. Okamoto, S. Ando, Japan Patent 2010.

[16] B.J. Lindberg, K. Hamrin, G. Johansson, U. Gelius, A. Fahlmann, C. Nordling, K. Siegbahn, Physica Scripta 1 (1970) 286.

[17] P. Vanattekum, J.M. Trooster, Physical Review B 18/8 (1978) 3872.

[18] J.F. Moulder, et. al., Handbook of x-ray photoelectron spectroscopy : a reference book of standard spectra for identification and interpretation of XPS data, 1995.

[19] V.G. Bhide, S. Salkalachen, A.C. Rastogi, C.N.R. Rao, M.S. Hegde, Journal of Physics D-Applied Physics 14/9 (1981) 1647.

[20] B.R. Strohmeier, D.M. Hercules, Journal of Catalysis 86/2 (1984) 266.

[21] T. Jiang, M.J.C. Brym, G. Dube, A. Lasia, G.M. Brisard, Surface & Coatings Technology 201/14 (2007) 6309.

[22] S.N. Alhajeri, N. Gao, T.G. Langdon, Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing 528/10-11 (2011) 3833.

[23] F. Huang, N.R. Tao, K. Lu, Journal of Materials Science & Technology 27/1 (2011) 1.

[24] L. Legrand, A. Tranchant, R. Messina, Electrochimica Acta 41/17 (1996) 2715.

Figure Captions

Fig. 1: Contents of Cl and S in Al coatings electrodeposited at various current densities from $DMSO_2$-$AlCl_3$ electrolytes with no additives. The contents were determined by XRF. ● and ○ denote the data for the electrolytes with the composition of $DMSO_2$: $AlCl_3$ = 10 : 2 and 10 : 3, respectively. Inset shows mole ratio of Cl to S in the Al coatings.

Fig. 2: XPS spectra of Al coating electrodeposited from $DMSO_2$-$AlCl_3$ electrolyte with no additives. The electrodeposition was performed at 60 mA cm^{-2} in the electrolyte with the composition of $DMSO_2$: $AlCl_3$ = 10 : 3.

Fig. 3: Contents of Cl and S in Al coatings electrodeposited from $DMSO_2$-$AlCl_3$ electrolytes containing 0-0.4 mol TMA. All the electrodeposition was carried out at 60 mA cm^{-2} in the electrolytes with the composition of $DMSO_2$: $AlCl_3$ = 10 : 3. The contents of Cl and S were determined by XRF. Each data point is the average of measurements for at least five different samples.

Fig. 4: XPS spectra of Al coating electrodeposited from $DMSO_2$-$AlCl_3$ electrolyte containing 0.4 mol TMA. The electrodeposition was performed at 60 mA cm^{-2} in the electrolyte with the

composition of $DMSO_2$: $AlCl_3$ = 10 : 3.

Fig. 5: Contents of Cl and S in Al coatings determined by XPS vs. Ar^+ ion etching time, comparing the Cl and S contents in Al coatings from the electrolytes without and with 0.4 mol TMA.

Fig. 6: SEM images of the surface of Al coatings electrodeposited from $AlCl_3$-$DMSO_2$ electrolytes ($DMSO_2$: $AlCl_3$ = 10 : 3) containing (a) 0, (b) 0.05, (c) 0.1, (d) 0.2 and (e) 0.4 mol TMA. The Al coatings were electrodeposited at 60 mA cm^{-2}.

Fig. 7: XRD patterns of Al coatings shown in Fig. 6.

Fig. 8: Vickers hardness of Al coatings electrodeposited from $AlCl_3$-$DMSO_2$ electrolytes ($DMSO_2$: $AlCl_3$ = 10 : 3) containing 0-0.4 mol TMA at 60 mA cm^{-2}. Each data point is the average of measurements for three different samples.

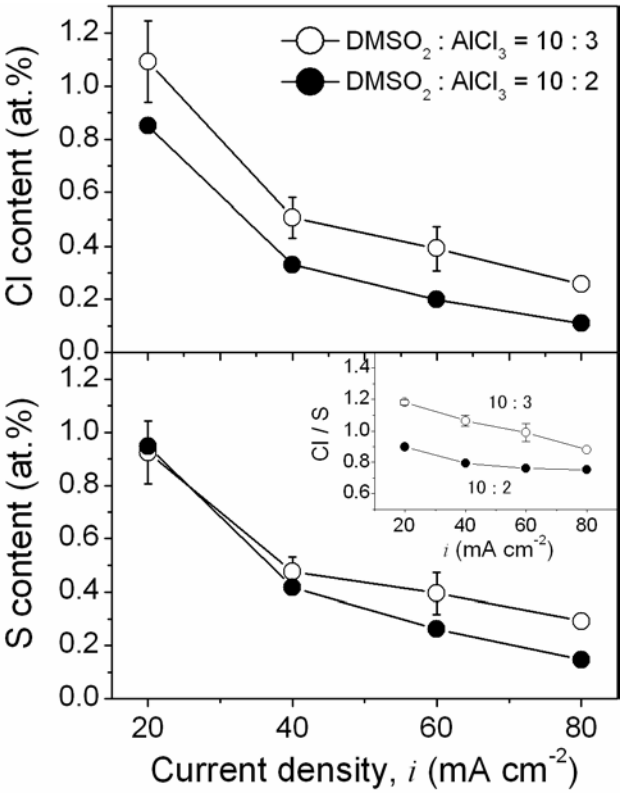
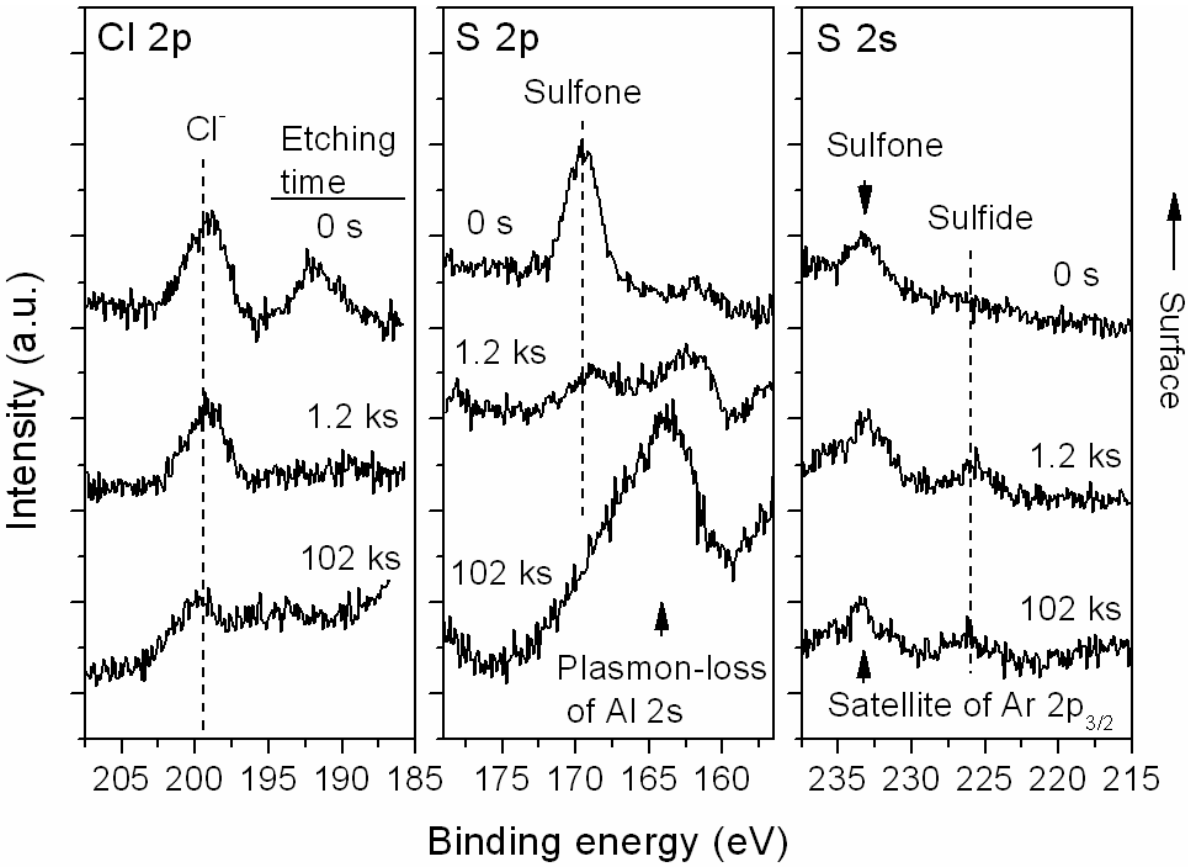


Fig. 1



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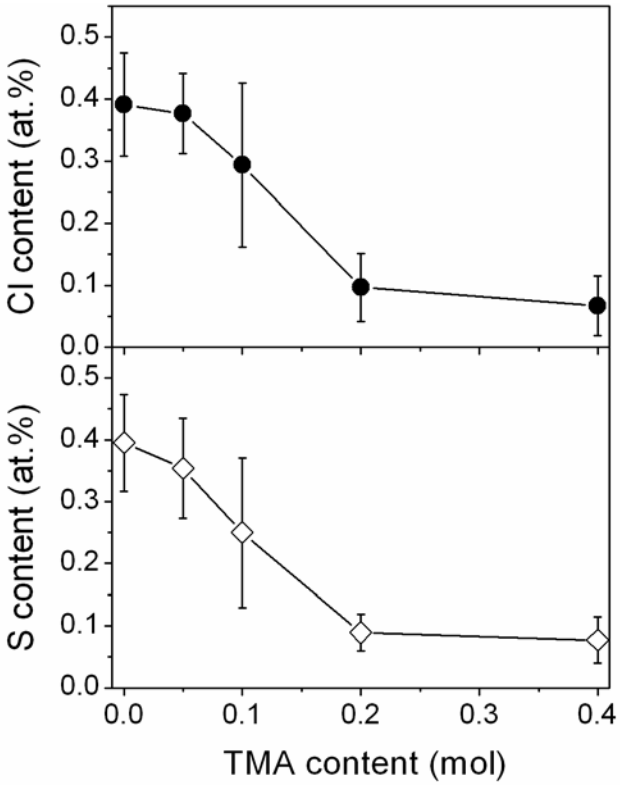

Fig.3

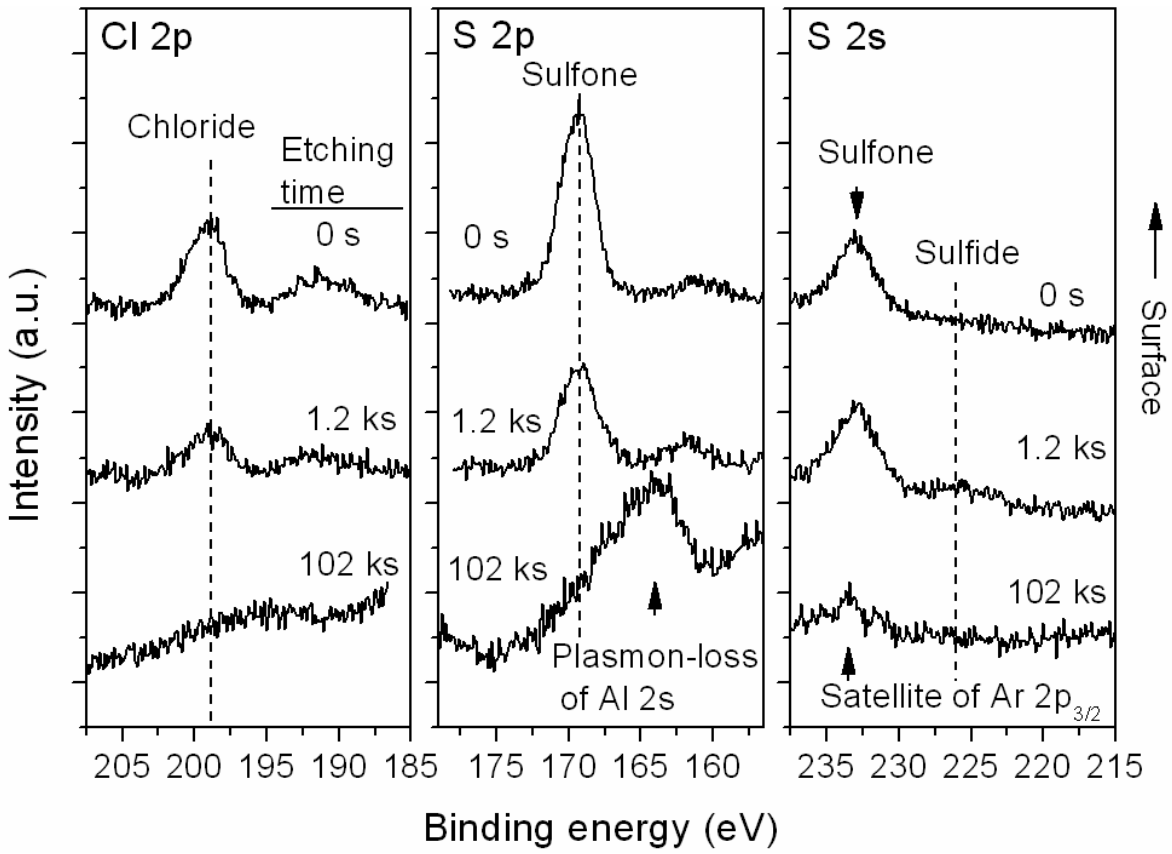

Fig. 4

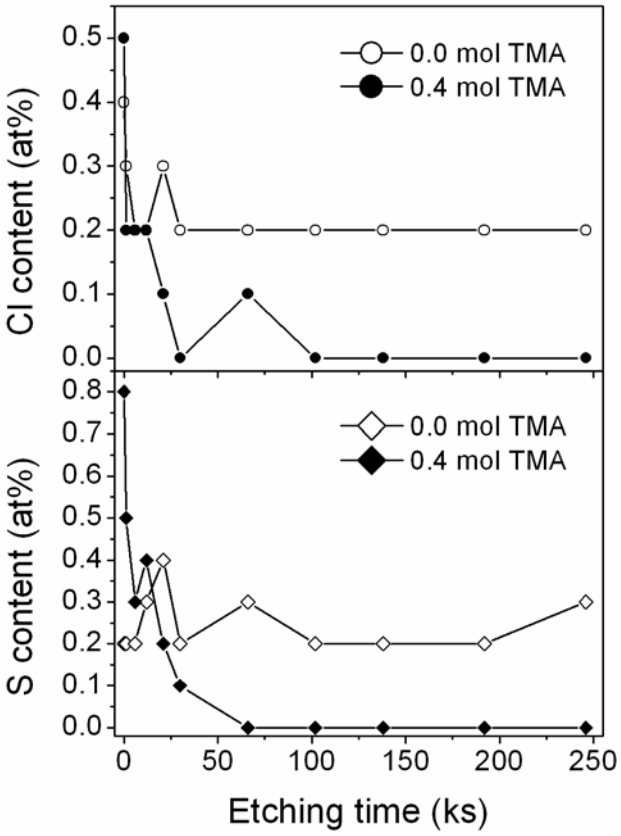

Fig. 5

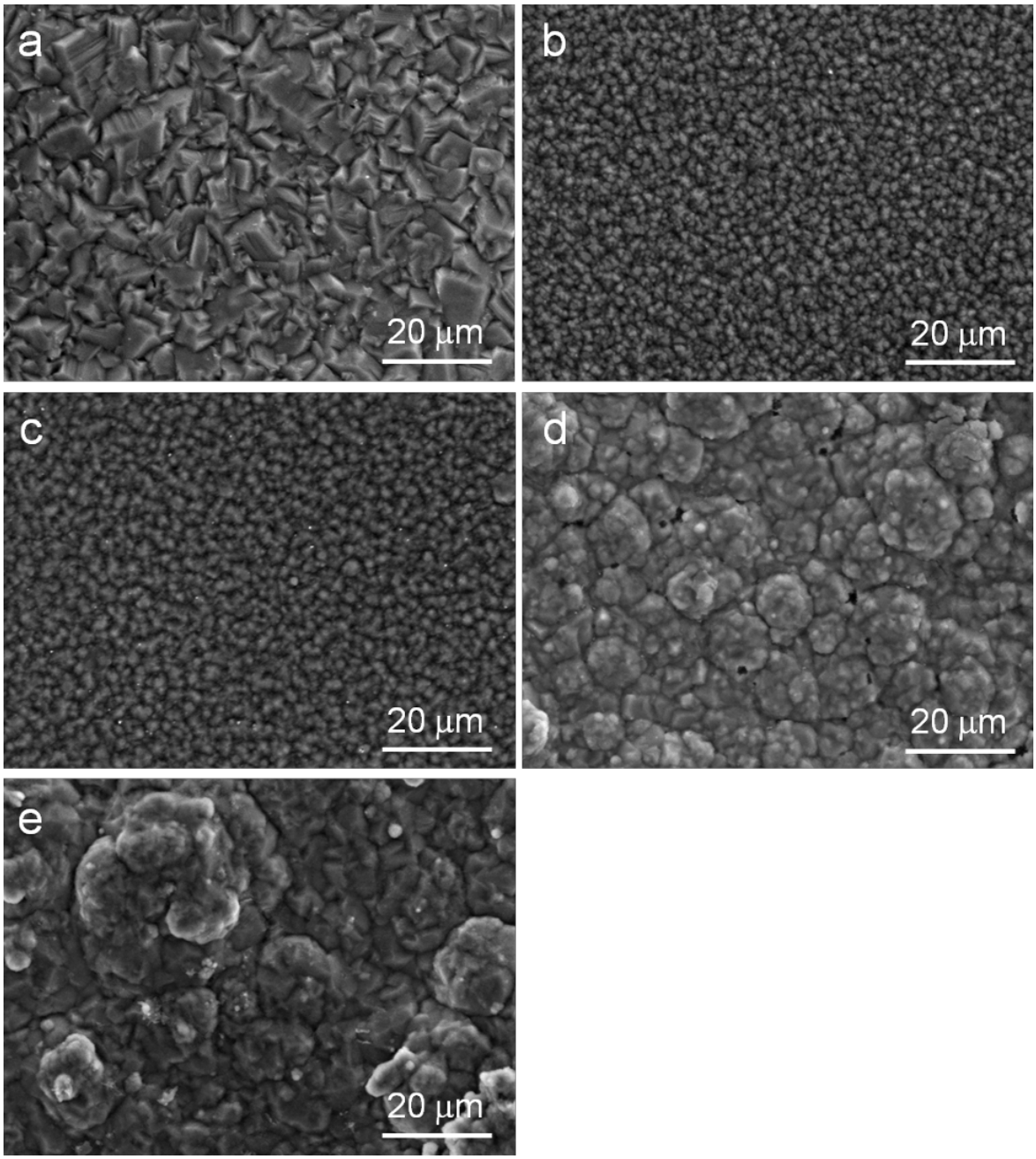

Fig.6

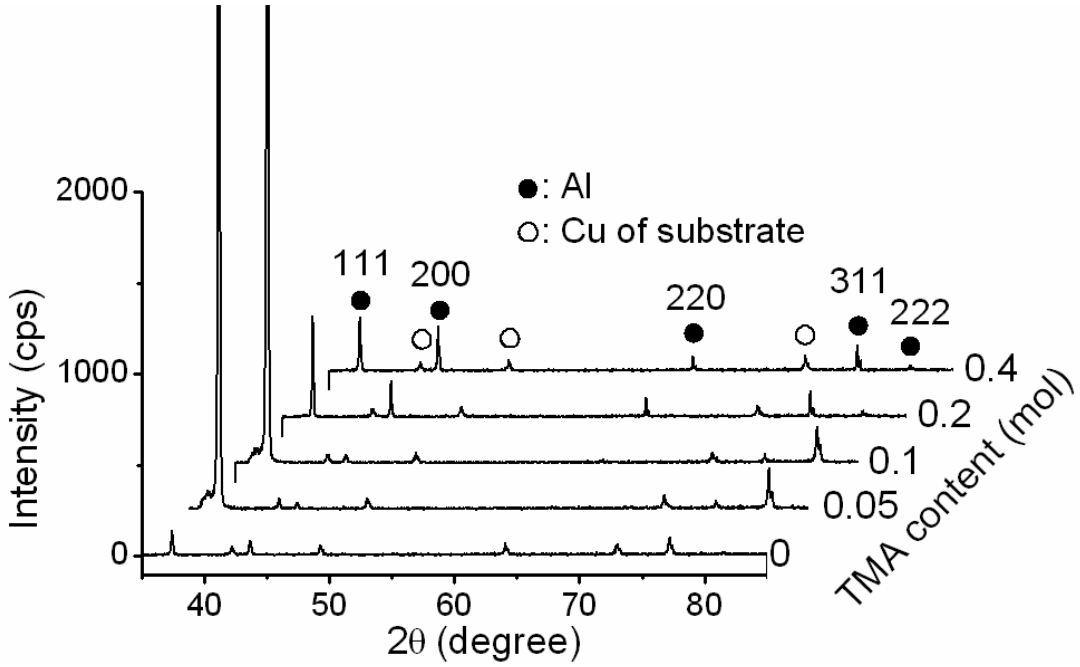

Fig. 7

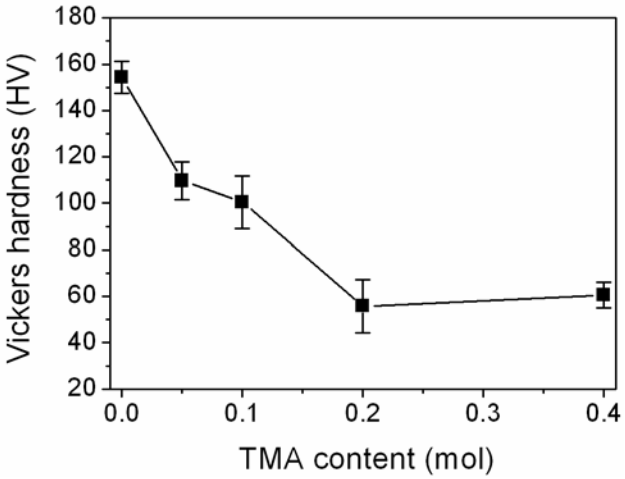

Fig. 8